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TECHNICAL REPORT

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⑥ TECHNICAL REPORT,

Compounds of High Nitrogen Content in Propellant Powders.

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SYNOPSIS

Since some success has already been achieved in the reduction of muzzle flash by the incorporation of compounds containing a high percentage of nitrogen such as dicyandiamide and nitroguanidine in propellant compositions it was considered desirable to extend this approach and to investigate other substances with comparatively high nitrogen content. In order to facilitate this investigation it was arranged that certain selected hydrazine derivatives be prepared at the Polytechnic Institute of Brooklyn under Picatinny Arsenal Contract No. X-762-Ord.-4254. Sixteen compounds were delivered for further study, and two additional compounds were synthesized at the Arsenal.

The substitution of hydrazine radicals for amino radicals in ammonia derivatives produces substances with considerably higher nitrogen content. Consequently a large portion of the compounds studied were chosen so as to form members of homologous series with a progressive increase in the number of hydrazine groups. It was found that progressive substitution of hydrazine radicals for amino and imino groups in guanidine causes, within the homologous series, an increase in sensitivity to impact, in brisance and in sensitivity to initiation, and a decrease in explosion temperature. The stability of these carbonic acid derivates, however, was not affected by the presence of hydrazine radicals. It was noted that the stability increased qualitatively, in this series, the higher the melting point.

Although the water solubility and stability of the majority of the compounds studied are such as to make them suitable for incorporation in propellant compositions, cyanuric hydrazide and 5-amino tetrazole are of the greatest interest because of their high nitrogen content. It is recommended that powders containing these two substances be prepared in order that their effectiveness as flash eliminating agents may be determined.

It was noted that guanidine perchlorate has properties which render it of interest as a possible replacement for ammonium nitrate/explosive compositions and that certain diamino- and triaminoguanidine salts are of possible interest as "cool" explosives.

~~SECRET~~
Compounds of High Nitrogen Content in Propellant Powder.

INTRODUCTION:

1. Some success has already been achieved in the development of flashless propellant powders by the incorporation of nitroguanidine or of dicyandiamide, both of which compounds are characterized by the fact that they possess a comparatively high nitrogen content, and a low carbon content. When flashlessness is obtained from powders containing such constituents, the smoke effects are favorable due to the reduced amount of carbon. It therefore appeared desirable to extend this approach and to investigate other substances with comparatively high nitrogen content as possible ingredients in propellant powders.

2. As a starting point it was decided to investigate hydrazine derivatives of carbonic acid and related compounds. If the explosive and stability characteristics of several members of the various homologous series which fall within this group could be obtained, an estimate of the utility of this class of compounds as possible propellant ingredients could be made. In order to facilitate such an evaluation it was arranged, Picatinny Contract No. W-762-Ord.-6264, that certain selected derivatives of hydrazine be prepared at the Polytechnic Institute of Brooklyn under the direction of Professor G. B. L. Smith. Twenty-one compounds were prepared of which sixteen were delivered to this Arsenal for further study. The work done at the Polytechnic Institute of Brooklyn also included the determination of certain physical properties such as the melting point and water solubility of these materials as well as a preliminary evaluation of their stability. The preparation of these compounds is described in Reference D. In addition to the substances prepared under Professor Smith's direction, two other compounds, guanidine perchlorate and cyanuric hydrazide were prepared at this Arsenal. This report covers the explosive and stability characteristics of these compounds.

OBJECT:

3. To determine the explosive and stability characteristics of certain selected compounds of high nitrogen content in order to estimate their utility as ingredients of propellant compositions.

RESULTS:

4. The physical properties of the compounds studied are recorded in Table I; the explosive and stability characteristics of these materials are recorded in Table II.

a. Sensitivity to impact (Bureau of Mines Apparatus using a 2 Kg. weight).

The Sensitivity to Impact Test value for triaminoguanidine perchlorate is similar to that of mercury fulminate (5 cm.). The values obtained in this test for guanyl azide nitrate and for azodicarbamidine dinitrate are close to that of PETN (17 cm.). The values for triaminoguanidine, formaldehyde nitroguanyl-hydrazone, acetaldehyde-nitroguanyl-

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hydrazone, diaminoguanidine nitrate and guanidine perchlorate are slightly greater than that for tetryl (46 cm.). The values for the compounds from nitroaminoguanidine and nitrous acid, cyanuric hydrazide, hydrazodicarbamide, azodicarbamide, aminoguanidine picrate, diaminoguanidine picrate, triaminoguanidine picrate, diguanazole oxalate, and 5-amino-tetrazole place these substances in the same class as TNT (100 f cm.) with respect to sensitivity to impact.

b. Brisance

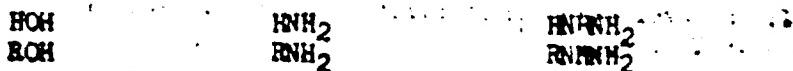
Diguanazole oxalate, cyanuric hydrazide and hydrazodicarbamide could not be initiated in the Sand Test, even when tetryl, was employed to booster the mercury fulminate initiating charge. Azodicarbamide and 5-amino-tetrazole required both tetryl and mercury fulminate to crush 1.7 and 4.7 grams of sand respectively. The brisance values of nitroaminoguanidine, formaldehyde nitroguanylhydrazone, acetaldehyde nitroguanylhydrazone, azodicarbamidino dinitrate, diaminoguanidine picrate, and triaminoguanidine picrate are similar to that of TNT. Triaminoguanidine perchlorate, guanidine perchlorate and guanyl azide nitrate are comparable to tetryl in their brisance values.

c. Stability

Hydrazodicarbamide, guanidine perchlorate, aminoguanidine picrate, diaminoguanidine picrate, triaminoguanidine picrate, diaminoguanidine nitrate, triaminoguanidine nitrate, diguanazole oxalate, cyanuric hydrazide and 5-amino tetrazole gave values in the 120°C. Vacuum Stability Test which indicate them to be comparatively stable. The following compounds gave values indicating them to be stable in either the 100°C. Heat Test or the 100°C. Vacuum Stability Test, but produced an excessive amount of gas in the 120°C. Vacuum Stability Test: Nitroaminoguanidine, formaldehyde nitroguanylhydrazone, acetaldehyde nitroguanylhydrazone, azodicarbamide, azodicarbamidine dinitrate, the compound from nitroaminoguanidine and nitrous acid and triaminoguanidine perchlorate. Guanyl azide nitrate showed a large weight loss in the 100°C. Heat Test, and therefore was not subjected to Vacuum Stability Tests.

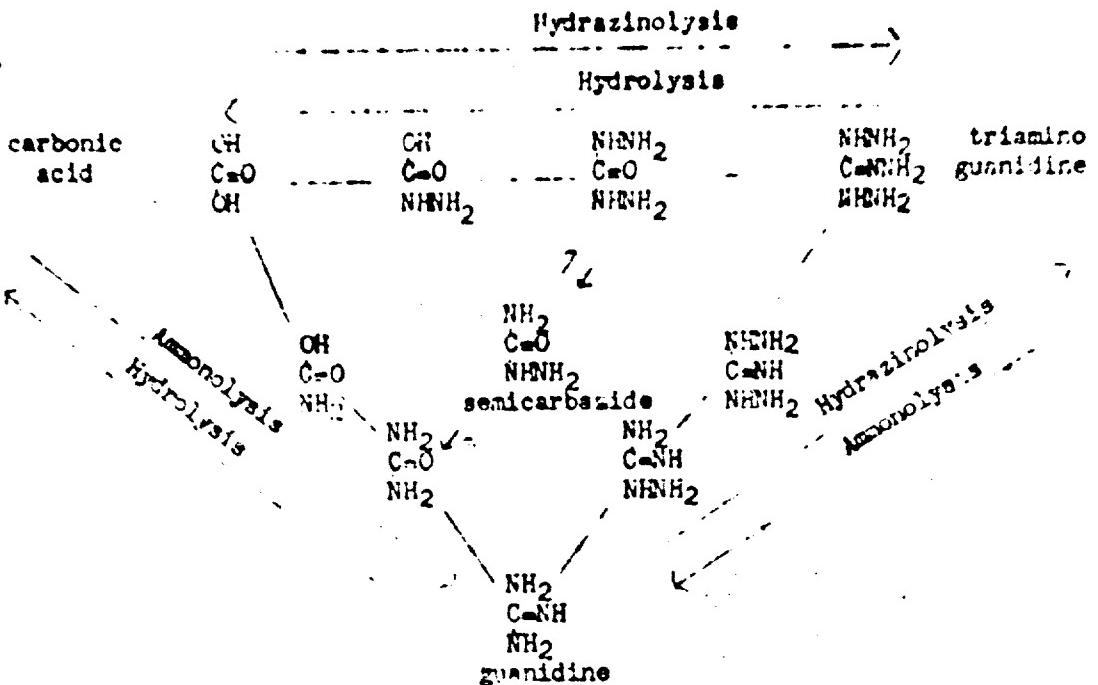
DISCUSSION
OF RESULTS:

5. Hydrazine, ammonia and water may all be looked upon as parent substances of systems of compounds in which the -NH_2 , -NH , and -OH groups may be considered analogous. In effect, this means that a wide variety of functional groups may be attached to these radicals to give compounds which are related to hydrazine and ammonia, respectively, in the same manner that ordinary oxygen compounds are related to water, as for instance:



where R is alkyl, aryl, acyl, metal, non-metal, etc. Just as water is capable of effecting reactions of hydrolysis, so ammonia and hydrazine are capable of acting as catalytic agents to effect reactions of ammonolysis and hydrazinolysis, respectively. In the case of derivatives of carbonic acid, these considerations become apparent by reference to the following diagrammatic representation illustrating these relationships: (Reference A)

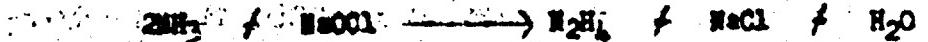
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- Hydrazine is a potential source of compounds of high nitrogen content since it contains 87.5% nitrogen. It is obvious that the partial or complete replacement of amino radicals in compounds such as urea and guanidine by the hydrazino group will give substances with still higher nitrogen contents as illustrated by the following table:

| Ammonia compound | Nitrogen percentage | Hydrazine compound | Nitrogen percentage |
|--|---------------------|--|---------------------|
| Urea $\text{H}_2\text{N}=\text{C}(=\text{O})\text{NH}_2$ | 46.65 | Semicarbazide $\text{H}_2\text{N}-\text{C}(=\text{O})-\text{NH}_2$ | 55.97 |
| | | Carbohydrazide $\text{H}_2\text{NNHC}(=\text{O})\text{NH}_2$ | 62.19 |
| Guanidine $\text{H}_2\text{N}=\text{C}(=\text{NH})\text{NH}_2$ | 71.14 | Aminoguanidine $\text{H}_2\text{N}-\text{C}(=\text{NH})-\text{NH}_2$ | 75.62 |
| | | Diaminoguanidine $\text{H}_2\text{NNHC}(=\text{NH})\text{NH}_2$ | 78.60 |
| | | Triaminoguanidine $\text{H}_2\text{NNHC}(=\text{NH})\text{NH}_2$ | 80.72 |

Hydrazine is commonly prepared by the oxidation of ammonia with hypochlorite:



The yield of this reaction is low and thus the cost of hydrazine at present is comparatively high. It is understood, however, that new synthetic methods have been developed which will materially reduce the price of hydrazine and

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thus make practical the consideration of hydrazine derivatives as ingredients in propellant compositions and in explosives. Since hydrazine will form hydrazoic acid upon treatment with nitrous acid and other oxidizing agents, its availability at a lowered price would be of considerable interest to the Ordnance Department.

6. The following table illustrates the effect of increasing the number of hydrazine linkages in carbonic acid derivatives on the Sensitivity to Impact Test values:

| <u>Compound</u> | <u>Formula</u> | <u>Sensitivity to Impact Test Bureau of Mines Apparatus, 2 kg.wt., cm.</u> |
|-------------------------------|--------------------------------|--|
| Guanidine nitrate | $C(NH_2)_3 NO_3$ | 100% (Ref.B) |
| Diaminoguanidine nitrate | $H_2NC(NHNH_2)_2 NO_3$ | 40 |
| Triaminoguanidine nitrate | $C(NHNH_2)_3 NO_3$ | 28 |
| Aminoguanidine picrate | $H_2NNHC(NH_2)_2 C_6H_2O_7N_3$ | 100% |
| Diaminoguanidine picrate | $H_2NC(NHNH_2)_2 C_6H_2O_7N_3$ | 80 |
| Triaminoguanidine picrate | $C(NHNH_2)_3 C_6H_2O_7N_3$ | 80 |
| Guanidine perchlorate | $C(NH_2)_3 ClO_4$ | 40 |
| Triaminoguanidine perchlorate | $C(NHNH_2)_3 ClO_4$ | 7 |
| Nitroguanidine | $H_2NC\overset{NH}{HN}O_2$ | 47 (Ref.C) |
| Nitroaminoguanidine | $H_2NN\overset{NH}{HN}O_2$ | 34 |

From the above data it may be seen that introduction of hydrazine radicals into the guanidine molecule increases the sensitivity to impact within a given homologous series. This is a structural effect which has not been recognized heretofore. It is probable that the essential feature of this increased sensitivity to impact involves the presence of a covalent nitrogen to nitrogen linkage in each hydrazine radical. A pertinent comparison involving a nitramine rather than a hydrazine radical may be made with guanidine nitrate and nitroguanidine, listed above, in which the formation of a nitrogen covalent bond in the latter compound increases the sensitivity to impact.

7. A qualitative relationship between the number of hydrazine radicals attached to the central carbon atom of carbonic acid and Sand Test characteristics may be noted from the following data:

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| Compound | Formula | Brisance, grams sand crushed upon initiation with 0.30 gm. Hg(CNC) ₂ | Millimolar brisance, Sand crushed per 0.001 mole |
|----------------------------------|--|--|---|
| Quanidine nitrate | C(NH ₂) ₃ NO ₃ | None (Ref.B) | - |
| Diaminoguanidine nitrate | H ₂ NH(NHNH ₂) ₂ NO ₃ | 27.8 | 10.5 |
| Aminoguanidine picrate | H ₂ NNHC(NH ₂) ₂ C ₆ H ₂ O ₇ N ₃ | 6.3 (21.1) ^a | 4.8 (23.7) ^a |
| Uranoguanidine picrate | H ₂ UC(NHNH ₂) ₂ C ₆ H ₂ O ₇ N ₃ | 40.6 | 30.5 |
| Triaminoguanidine picrate | C(NHNH ₂) ₃ C ₆ H ₂ O ₇ N ₃ | 44.0 | 35.6 |
| Guanidine perchlorate | C(NH ₂) ₃ ClO ₄ | 51.6 | 20.6 |
| Triaminoguanidine perchlorate | C(NHNH ₂) ₃ ClO ₄ | 51.0 | 26.2 |
| Nitroguanidine | H ₂ N _x NHNO ₂ | 33.4 (Ref.C) | 8.7 |
| Nitroaminoguanidine | H ₂ NNH _x NHNO ₂ | 44.5 | 13.2 |

^aInitiated with 0.25 gm. Hg(CNC)₂ and 0.25 gm. tetryl.

The only apparent exception to the generalization that an increase in hydrazine residues causes a increase in sand crushed is found in the case of guanidine and triaminoguanidine perchlorates. This anomaly is eliminated, however, if comparison is made on an equimolar basis rather than a weight basis; inspection of the millimolar brisance values clearly shows that molecule for molecule triaminoguanidine perchlorate crushes more sand than guanidine perchlorate. Mention should also be made of the fact that the oxygen balance of the guanidine derivative is more favorable than that of the triaminoguanidine derivative, this effect obscuring the increased brisance conferred by hydrazine radicals. As in the case of sensitivity to impact, it is probable that the pertinent consideration in the case of brisance is the increase in covalent nitrogen to nitrogen linkages, and reference is again made to the increased brisance of nitramines as opposed to amine nitrates. Although the effect of hydrazine radicals is not as striking in the case of sensitivity to initiation as with brisance, nevertheless several interesting observations may be made. Diamino and triaminoguanidine picrates can be initiated by mercury fulminate alone, but aminoguanidine picrate with but one nitrogen to nitrogen linkage requires both tetryl and mercury fulminate to effect complete initiation. A further comparison may be made with nitroguanidine, which requires a tetryl booster for initiation (Ref.C) and nitroaminoguanidine which can be initiated by mercury fulminate alone. The foregoing generalizations should aid materially in predicting brisance, sensitivity to initiation and sensitivity to

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Impact of compounds containing nitrogen to nitrogen links.

8. The stability data for the salt type derivatives of carbonic acid, given in the following table, indicate that despite the increased sensitivity to impact, brisance and sensitivity to initiation conferred by the introduction of hydrazine residues, only a slight decrease in stability is produced by the presence of this radical.

| | Loss in weight after 90 hours | | Vacuum Stability Tests | | | | Melting point, °C. | |
|-------------------------------|----------------------------------|---------------------|------------------------|-----------------|---------|-----------|--------------------------|--|
| | at 80°C. and 90 hours at | 100°C. ^a | 100°C. | | 120°C. | | | |
| | | | cc. gas | hrs. | cc. gas | hrs. | | |
| Guanidine nitrate | - | - | - | - | 0.23 | 40 (RaI3) | 212 | |
| Diaminoguanidine nitrate | Nil | 0.77 | 40 | 1.92 | 40 | | 142-144 | |
| Triaminoguanidine nitrate | 0.31 | - | - | 1.06 | 40 | | 216-217 | |
| Aminoguanidine picrate | Nil | 0.20 | 40 | 0.37 | 40 | | 183-184 | |
| Diaminoguanidine picrate | 0.19 | 0.02 | 40 | 0.48 | 40 | | 188-190 | |
| Triaminoguanidine picrate | 0.70 | 0.43 | 40 | 1.45 | 40 | | 170-172 | |
| Guanidine perchlorate | - | 0.36 | 40 | 1.16 | 40 | | 240 | |
| Triaminoguanidine perchlorate | 3.53 | 0.68 ^b | 40 | 11 ^b | 23 | | 128 | |

^aDetermined at the Polytechnic Institute of Brooklyn.

^b1.00 gm. sample used.

Within the nitrate and picrate series it may be seen that a slight increase in gas evolution in the 120°C. Vacuum Stability Test is obtained as hydrazine is progressively introduced. The test values of all of these derivatives, however, indicate them to be of acceptable stability. Triaminoguanidine perchlorate is definitely less stable than guanidine perchlorate, but it is to be pointed out that the melting point of triaminoguanidine perchlorate is 128°C., being much closer to the temperature of the test than in the case of guanidine perchlorate. Many explosives are unstable near their melting points, tetryl being an example of this type of behavior. It appears more reasonable to assign the major cause of the comparative instability of triaminoguanidine perchlorate to its low melting point rather than to the presence of hydrazine radicals. Inspection of the data in the above table indicates that, within a given series, the member with the lowest melting point produces the most gas in the 120°C. Vacuum Stability Test; the melting point however, bears no relationship to the number of hydrazine residues present.

9. The following data for nitroguanyl hydrazine derivatives indicate that although the sensitivity to impact, brisance and sensitivity to initiation of nitroaminoguanidine are not materially changed by condensation with carbonyl compounds, the stability characteristics are affected by hydrazone formation.

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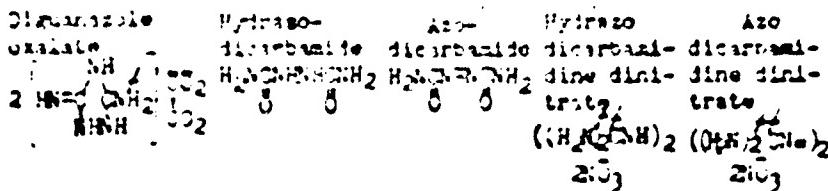
| | Nitroguani- dine | Nitroamino- guanidine | Formaldehyde nitroguanyl- hydrazone | Acetalde- nitro- guanyl- hydrzone | Acetone nitro- guanyl- hydrzone ² |
|--|-------------------------------------|--------------------------------------|--|---|---|
| | $\text{H}_2\text{NCONHNHO}_2$ NH | $\text{H}_2\text{NNHCNHCNO}_2$ NH | $\text{CH}_2=\text{C}(\text{NO}_2)\text{NH}$ | $\text{CH}_3\text{CH}=\text{C}(\text{NO}_2)\text{NH}$ | $(\text{CH}_3)_2\text{C}=\text{NHCNO}_2$ NH |
| Sensitivity to Impact, cm. | 47 | 34 | 34 | 33 | |
| Brisance | 33.4 | 44.5 | 45.4 | 44.3 | |
| Sensitivity to Initiation, gm. Hg(CNC) ₂ | | 0.25 | 0.25 | 0.23 | |
| Weight Loss after 90 hours at 80°C. and 90 hours at 100°C. ³ | | 0.60 | 39.1 | 2.0 | 65.4 |
| 100°C. Vacuum Stability Test: cc. gas | | 0.85 | | .69 | |
| hours | | 40 | | 40 | |
| 120°C. Vacuum Stability Test: cc. gas | 0.37 | 114 | 114 | 114 | |
| hours | 40 | 40 | 16 | 24 | |
| Melting point, °C. | 247 | 185 | 165 | 180 | 160 |

¹Data from Ref.C.²Determined at the Polytechnic Institute of Brooklyn.³1.00 gm. sample used.

It is evident that replacement of an amino group in nitroguanidine by a hydrazine group to form nitroaminoguanidine causes a reduction in stability as measured by the 120°C. Vacuum Stability Test. The formation of the hydrazone linkage still further reduces the stability of this type of compound. The members of this series with the lower melting points are the least stable thermally, just as in the case of the salt type derivatives mentioned previously.

10. The remaining compounds studied form only incomplete series of else bear no structural relation to one another. Diguanazole oxalate a cyclic compound, and hydrazodicarbamide, azodicarbamide and azodicarbanidine dinitrate, open chain compounds, may all be considered to be symmetrical disubstituted hydrazines, the hydrazine group in the latter two being oxidized. The following data indicate the effect of combination with the nitrate ion in decreasing the stability characteristics of this type of compound when compared with the non-ionic substances or the oxalate compound.

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| Sensitivity to Impact. | 95 | 100 ^a | 95 ^a | 18 |
|--|------|------------------|-----------------|--------------------|
| Brigance 100°C. Vacuum | Nil | Nil | 1.72 | 42.5 ^b |
| Stability Test, cc. in 40 hrs. 120°C. Vacuum | 0.40 | 0.30 | 0.73 | 6.57 |
| Stability Test, cc. in 40 hrs. Loss in weight after 90 hours at 80°C. and 90 hours at 100°C. ^c | 0.55 | 0.36 | 5.60 | 10.77 ^c |
| Melting point,°C. Over 250 | 0.31 | 0.85 | 0.39 | 21.76 |
| | 246 | 223-226 | 136 | 0.66 |
| | | | | 179.5 |

^aInitiated with 0.25 gm. $\text{Hg}(\text{CN})_2$ and 0.25 gm. tetryl.

^bInitiated with 0.30 gm. $\text{Hg}(\text{CN})_2$.

^c1.00 gm. sample.

^dDetermined at Polytechnic Institute of Brooklyn.

It is of interest to note that oxidation of the hydrazine radical in hydrazodicarboxide to an azo group induces slight explosive properties, but renders the resulting compound slightly less stable, as indicated by the 120°C. Vacuum Stability Test values. The oxidation of a hydrazine linkage to an azo group, however, produces the opposite effect on stability in the case of hydrazodicarbamide dinitrate which is much less stable than azodicarbamide dinitrate. Inspection of the above data reveals that in the case of the disubstituted hydrazine derivatives listed, a low melting point is characteristic of the less stable substances, suggesting again that this physical property rather than the presence of a hydrazine group largely determines the stability of these compounds. Cyanuric hydrazide, which is a trihydrazino symmetrical 1, 3, 5-triazine, is indicated on the basis of the explosive and stability tests (Table II) to be non-explosive and to have excellent stability. It is interesting to note that trinitromethylaniline which may be considered to be trinitro-amino symmetrical triazine is about as brisant as TNT and is stable in the 134.5°C. Heat Test (Ref. 8). In the case of these two triazine derivatives, at least, the introduction of substituents containing a covalent nitrogen to nitrogen linkage has not caused impairment of the stability. Evidently the effect of three hydrazine residues upon the cyanuric group is not sufficient to cause cyanuric hydrazide to be brisant. The compound 5-amino tetrazole, which bears no direct structural relationship to any of the other compounds studied but is obtainable by diazotisation of aminoguanidine shows a remarkable stability with a 120°C. Vacuum Stability Test value of 0.09 cc. in 40 hours. This value suggests that reasonable stability may be expected from other com-

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bers of the tetrazole series.

11. Preliminary tests of guanyl azide nitrate at the Polytechnic Institute of Brooklyn indicated it to be unstable, its weight loss after 90 hours at 80°C. being 12.81%. Since guanyl azide may be isomerized to 5-amino tetrazole, and thus bears a direct synthetic relationship to this compound, it was considered of interest to determine the explosive properties of its nitrate. The brisance value of 55.2 for guanyl azide nitrate shows that this compound approaches PETN in this characteristic. The instability of this compound may be compared with the rather low stability of azodicarbamidine dinitrate which may be considered to be a diguanyl nitrate linked to two doubly bound nitrogen atoms. Five of the twenty-one compounds prepared at the Polytechnic Institute of Brooklyn were considered to be unsuitable for further investigation. Of these, hydrazodicarbamidine dinitrate and acetone nitroguanylhydrazone have already been mentioned. The preparation of urea azide was undertaken in view of the interesting properties found for 5-amino tetrazole and guanyl azide nitrate. The compound when prepared, however, was found to undergo decomposition at room temperature with the evolution of hydrazoic acid. The benzaldehyde derivative of triaminoguanidine, a trihydrazone, had a weight loss in 90 hours at 80°C. of 8.9%, thus further confirming the thermal instability found for this type of derivative in the case of the nitroguanylhydrazone. In the course of the preparation of triaminoguanidine perchlorate it was found that a dipercchlorate was also formed. This type of compound was unanticipated, and as far as is known is the only case where triaminoguanidine functions as a diacidic base. Because of its low melting point (85-90°C.) and large water solubility no additional tests were made with this substance.

12. The following data indicate the effect of progressive introduction of hydrazine radicals into the carbonic acid molecule upon the Decomposition Temperature; it is also of interest to note that the relation between this temperature and the melting point of the explosives is much less well defined than the relation between stability and melting point.

| <u>Compound</u> | <u>Five second Decomposition Tem- perature, °C.</u> | <u>Melting Point, °C.</u> |
|-------------------------------|---|---------------------------|
| Guanidine nitrate | 305 ^a | 212 |
| Diaminoguanidine nitrate | 290 | 142-144 |
| Triaminoguanidine nitrate | 260 | 216-217 |
| Aminoguanidine picrate | 290 | 183-184 |
| Diaminoguanidine picrate | 250 | 188-190 |
| Triaminoguanidine picrate | 215 | 170-172 |
| Guanidine perchlorate | 365 | 240 |
| Triaminoguanidine perchlorate | 270 | 128 |
| Nitroguanidine | 275 (Ref.C) | 247 |
| Nitroaminoguanidine | 220 | 185 |

^aDetermined during this investigation.

Inspection of the above data shows that within a given homologous series the introduction of a hydrazine group lowers the Decomposition Temperature Test.

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value. It is to be mentioned, however, that none of the substances in the foregoing list have a dangerously low decomposition temperature, and indeed the only substance studied with an excessively low value is guanyl azide nitrate with a value of 140°C.

13. Some preliminary consideration has been given to the possible use of the various materials studied as ingredients of propellant compositions. Aside from the special requirement of the present investigation that a compound must have a high nitrogen content, there are certain general requirements for ingredients of propellants. Firstly, the compound must not be unstable, nor must it render nitrocellulose unstable. Secondly, it must not be appreciably water soluble, since in the water-dry treatment used in the manufacture of smokeless powder, substances which are soluble in water may be leached from the powder. If it is considered that a loss in the 100°C. Heat Test of less than 1.0% is satisfactory, then all the compounds studied, with the exception of guanyl azide nitrate, are of suitable stability. Because of their comparatively large 120°C. Vacuum Stability Test values the nitroguanylhydrazones of formaldehyde and acetaldehyde and azodicarbamidine dinitrate may be too unstable, but this conclusion cannot be definitely established in the absence of knowledge of the relationship between stability of additives and of smokeless powder containing the same additives. Formaldehyde and acetaldehyde nitroguanylhydrazones being organic in nature are interesting in that their water solubility is low and their solubility in organic solvents is appreciable. These aldehyde derivatives may be expected to be physically compatible with nitrocellulose and may exert some plasticizing action since they would probably behave as hydrogen bonding agents (Ref.F). Guanidine and triaminoguanidine perchlorates, diamino and triaminoguanidine nitrates would be eliminated from consideration on the basis of their water solubility. The picrates of amino, diamino and triaminoguanidine do not contain sufficient nitrogen to warrant their consideration for the present purpose, the nitrogen content of triaminoguanidine picrate being 37.3%; these materials were investigated in order that data concerning the explosive characteristics of another homologous series of hydrazine derivatives might be obtained and because of possible utility as high explosives rather than as propellant ingredients. This then leaves for consideration the following compounds: The reaction product of nitrous acid and nitroaminoguanidine, nitroaminoguanidine, formaldehyde and acetaldehyde nitroguanylhydrazones, diguanazole oxalate, cyanuric hydrazide, 5-amino tetrazole, hydrazodicarbamide, azodicarbamide, azodicarbamide and azodicarbamidine dinitrate. Of these substances cyanuric hydrazide with 73.6% nitrogen and 5-amino tetrazole with 82.3% nitrogen appear to be of considerably greater interest than the other substances, all of which have a smaller nitrogen content. A further advantage which 5-amino tetrazole possesses is that it has a small brisance (Table II) which is probably indicative of its ability to increase the ballistic potential of a powder containing it. Its large negative heat of formation (-57.1 K cals.) renders it of interest as a propellant ingredient, since considerably more energy could be obtained from it than from nitrogunidine with a heat of formation of 18.0 K cals.

14. Nitrogunidine and dicyandiamide both contain four atoms of hydrogen and four atoms of nitrogen per molecule. If consideration of possible high nitrogen compounds is restricted to those with no more atoms of hydrogen than nitrogen so that no more ammonia will be formed than is the case with dicyan-

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diamide or nitroguanidine, then the number of available compounds is reduced to a large extent. To reduce the possibility of smoke being formed, it appears reasonable to consider only those compounds with one or two carbon atoms, since dicyandiamide has but two carbon atoms per molecule. A perusal of the formula index of Beilstein's Handbuch der Organischen Chemie reveals that the majority of substances which contain better than 60% nitrogen, and which contain no more hydrogen atoms than nitrogen atoms are cyclic and belong to either the triazole or tetrazole series. The following compounds are representatives of these classes: tetrazole, 5-amino tetrazole, 5-cyano tetrazole, hydrazino triazole, guanazole and methyl tetrazole. The only non-gaseous substances meeting these requirements which belong to the open chain series are compounds such as carbonic acid diazide CO_2N_2 and cyanazide, both of which are extremely sensitive and unstable. It is true that guanidines, an open chain compound contains 71% nitrogen, and derivatives such as amino, diamino and triamino guanidine will contain still higher percentages of nitrogen. None of these compounds, however, can exist in the free state due to their strongly basic nature, and are available only in the form of salts. Thus the nitrogen percentage will be reduced, unless the anion contains nitrogen also. The azides of this series are unknown except for guanidine azide (Ref.I). A further difficulty with guanidine derivatives in general is their water solubility, guanidine azide being soluble to the extent of 159.2 gm. per 100 gm. of water. These difficulties will be present also with amidines, such as azodicarbamidine, which also exist as salts. Thus the most promising type of compound for future study appears to be cyclic hydrazine or hydrazoic acid derivatives which fall chiefly within the triazole and tetrazole classes. Of those compounds investigated during the present study 5-amino tetrazole and cyanuric hydrazide best meet the requirements developed above.

15. Although the primary object of this investigation was concerned with the possible use of the compounds studied as propellant ingredients, it was considered to be of interest to evaluate these high nitrogen compounds as high explosives. The Sand Test value of triaminoguanidine perchlorate (Table II), places it in the same class as Haleite and tetryl, but its extreme sensitivity to impact and its instability in the 120°C. Vacuum Stability Test militate against its consideration as a military explosive. Since guanidine perchlorate has a better oxygen balance than triaminoguanidine perchlorate, and in view of the use of perchlorate compounds in commercial explosives, it was believed of interest to investigate its explosive properties, despite the fact that it does not fall strictly within the class of high nitrogen compounds under consideration. The possibilities of guanidine perchlorate have been mentioned previously, it having been described by Stettbacher (Ref.G) as being superior to picric acid. The brisance value of 51.6 found for guanidine perchlorate shows that it also is comparable with Haleite and tetryl. Its Sensitivity to Impact Test value of 40 cm. indicates that it is not unduly sensitive and its 120°C. Vacuum Stability Test value of 1.16 cc. in 40 hours is sufficiently low so that its stability may be considered satisfactory. Its melting point, 240°C., precludes its use as a cast explosive by itself. The chief objection to the use of this explosive is its water solubility. Since this same objection may be raised against ammonium nitrate, and since mixtures of guanidine perchlorate and TNT would be far more brisant than Amatols of the same composition, mixtures of this explosive with TNT might be more acceptable than Amatols. Should the cost of guanidine salts and perchloric acid become sufficiently low, the further investigation of this compound would appear to be de-

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sirable. For purposes such as bursting charges for chemical shell or other uses where the ignition of flammable materials is not desired, an explosive which attains a comparatively low temperature on explosion is indicated. A cool explosive which at the same time is brisant would be particularly useful. Nitroguanidine has been used as an ingredient of cool explosives as also has guanidine picrate (Ref.H). It appears reasonable to assume that other nitrogenous derivatives of carbonic acid such as those considered in the present investigation may also be of interest as cool explosives. The following compounds are reasonably stable and are sufficiently brisant to warrant consideration for this purpose: Nitroamino guanidine, diamino and triaminoguanidine picrates, triaminoguanidine nitrate and guanidine perchlorate.

CONCLUSIONS:

16. It is concluded that progressive introduction of hydrazine radicals into the carbonic acid molecule causes, within a homologous series, an increase in sensitivity to impact, brisance, sensitivity to initiation and a decrease in decomposition temperature. No decrease in stability attributable to the presence of hydrazine groupings is occasioned by an increase in the number of these groups present in carbonic acid derivatives. The stability of these compounds increases qualitatively, the higher the melting point.

17. It is concluded that the following compounds are sufficiently stable and sufficiently insoluble in water for inclusion in propellant compositions: The reaction product of nitrous acid and nitroamino guanidine, nitroamino guanidine, formaldehyde and acetaldehyde nitroguanylhydrazone, diguanazole oxalate, cyanuric hydrazide, 5-amino tetrazole, hydrazodicarbamide, azodicarbamide and azodicarbamidine dinitrate. Of these substances cyanuric hydrazide with 72.6% nitrogen and 5-amino tetrazole with 82.3% nitrogen appear to be of considerably greater interest than the other substances since all others have a smaller nitrogen content.

18. It is concluded that guanidine perchlorate offers some promise as a high explosive, because its brisance is of the same order of magnitude as Haleite and tetryl, its stability is satisfactory and it is not unduly sensitive to impact. It is also concluded that the nitrates and picrates of diamino and triaminoguanidine which have brisance values close to that of INT, offer promise as cool explosives.

RECOMMENDATIONS:

19. It is recommended that powders containing 5-amino tetrazole, and cyanuric hydrazide be prepared to determine whether flashlessness with improved smoke effects can be attained by the use of these high nitrogen compounds. If this object is achieved, then powders containing other compounds of high nitrogen content, should be prepared.

20. It is recommended that the explosive and stability characteristics of other high nitrogen compounds, particularly those of the triazole and tetrazole series, be determined if improved smoke and flash effect are ob-

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tained by incorporating in propellant powders the compounds mentioned in the preceeding paragraph.

EXPERIMENTAL
PROCEDURE:

21. The preparation of guanidine perchlorate was accomplished as follows: To 13 grams of guanidine carbonate dissolved in 40 cc. of water was added slowly with stirring 17.3 cc. of 70% perchloric acid. After filtration, the solution was evaporated to dryness on the steam bath and was recrystallized from a mixture of 100 cc. absolute alcohol and 50 cc. of benzene. The yield was nearly quantitative.

22. Cyanuric trihydrazide was prepared by the following procedure: Cyanuric chloride (64.7 grams) was partly dissolved in 250 cc. of acetonitrile and to this mixture was added with cooling in an ice bath and stirring 150 cc. of 85% hydrazine hydrate and 100 cc. of alcohol. The white precipitate which was formed was collected on a Buchner funnel, washed with three 100 cc. portions of alcohol and two 100 cc. portions of water. The yield after drying was 57.5 grams or 95.8%.

23. The Sensitivity to Impact, Explosion Temperature, Vacuum Stability, 1000°C. Heat and Sand Tests were performed according to procedures standard at this Arsenal, except that in the Explosion Temperature and Vacuum Stability Tests of triaminoguanidine perchlorate smaller size samples than standard were used as indicated in the footnotes to Table II.

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Table I

Physical Properties of High Nitrogen Compounds.

| Compound | Melting Point °C. | pt. of Satur- ated Solution at 25.46°C. | Solubility | Heat of Combus- | Heat of Formation |
|---|----------------------|---|---|---|---|
| | | | In water, g./ 100 g. solvent volume | tion at constant pressure cal./g. | at constant at constant Kg. cal./mole |
| Guanidine Perchlorate | 240 | | Very soluble | | |
| Aminoquandine Picrate | 183-184 | | 0.36 | | |
| Diisoguanidinium Picrate | 188-190 | | 0.29 | | |
| Diacetoguanidinium Nitrate | 142-144 | | Very soluble | | |
| Triacetoguanidinium Picrate | 170-172 | | 0.54 | | |
| Triaminoguanidinium Nitrate | 216-217 | 4.50 | Very soluble | 2399 | 1.0 |
| Triaminoguanidinium Perchlorate | 128 | 4.37 | | | |
| Nitroguanidinium | 185 | 5.02 | Very soluble | | |
| Formaldehyde Nitroguanylylhydrazone | 165 | 4.50 | 1.16 | | |
| Acetaldehyde Nitroguanylylhydrazone | 180 | 4.27 | 0.26 | | |
| Hydrazosdicarbamides | 246 | 5.76 | 0.64 | | |
| Azodicarbamide | 223-226 | 5.87 | 0.12 | | |
| Azodicarbamidine Dinitrate | 179.5 | 2.37 | 0.39 | | |
| Compound from Mitroguanidines and Nitrous Acid | 234 | 4.16 | 0.39 | | |
| Guanyl Aside Nitrate | 126-127 | | Very soluble | | |
| Cyanuric Hydrate | Over 300 | | | | |
| Diguaniisoic Oxalate | Over 250 | | | | |
| γ -Amino tetraazole | 202-203 | 3.44 | | 2.16 | - 57.1 |
| | | | | 2992 | |

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Table II

Explosive and Stability Characteristics of High Nitrogen Compounds.

| Test | Guanidine Piclorate | Aminoguanidine Picrate | Diamino Guanidine Picrate | Triamino Guanidine Nitrate | Triaminoguanidine Perchlorate |
|---|---------------------|--|---------------------------|----------------------------|--------------------------------------|
| Sensitivity to Impact, 2 Kg. wt. sand shell. | 40 | 100 | 40 | 80 | 28 |
| Sag Test | | | | | 7 |
| Brisance, gms. sand crushed | | | | | |
| Initiated with: | | | | | |
| 0.30 g. Hg(OAc) ₂ | 31.6 | 6.3 | 40.6 | 27.8 | 44.0 |
| 0.25 g. Hg(OAc) ₂ | | | | | |
| 0.25 g. tetryl | | | | | |
| Sensitivity to Initiation: gms. Hg(OAc) ₂ | 0.25 | 0.10 gm. tetryl 0.25 gm. Hg(OAc) ₂ | 0.25 | 0.25 | 0.25 |
| Decomposition Temperature | | | | | |
| Temp. to cause decom. in 5 sec. °C. | 365 | 290 | 250 | 290 | 215 |
| 100°C. Heat Test | | | | | 260 |
| Loss, first 48 hrs., % | 0.07 | 0.15 | 0.02 | 0.15 | 0.38 |
| Loss, second 48 hrs., % | 0.00 | 0.05 | None | 0.02 | 0.01 |
| Explosion in 100 hrs. | None | None | None | None | None |
| 100°C. Vacuum Stability Test cc. gas hours | 0.36 | 0.20 | 0.02 | 0.77 | 0.43 |
| 120°C. Vacuum Stability Test cc. gas hours | 40 | 40 | 40 | 40 | 40 |
| 2. 0.01 gm. sample used. | | | | | |
| | | b 1.00 gm. sample used. | | | c Very close to Hg(OAc) ₂ |

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Table II (Continued)

| Explosive and Stability Characteristics of High Nitrogen Compounds ^a . | | | | | |
|---|-----------------------|--------------|--------------|-----------------------|----------------|
| | Mitroguanyl-guanidine | Formaldehyde | Acetaldehyde | Nitro vinyl-hydrazide | Azodicarbamide |
| Sensitivity to Impact, Kg. wt. ^b | 34 | 33 | 100 | 4 | 45 |
| cm. fall. | | | | | 18 |
| Sand Test, gm. sand crushed | | | | | |
| Initiated with: | | | | | |
| 0.30 g. Hg(OAc) ² | 44.5 | 45.4 | 44.3 | None | None |
| 0.25 g. Hg(OAc) ² | | | | | |
| 0.25 g. tetryl | | | | | |
| Sensitivity to Initiation: gm., Hg(OAc) ² | 0.25 | 0.25 | 0.23 | | 0.23 |
| Decomposition Temperature, Temp. to cause decompr. in 5 sec., °C. | 220 | 190 | 210 | 320 | 285 |
| 100°C. Heat Test: Loss, first 48 hrs., % | 0.23 | 0.93 | 0.33 | 0.19 | 0.24 |
| Loss, second 48 hrs., % | 0.10 | 0.44 | 0.19 | 0.05 | 0.11 |
| Explosion in 100 hrs. | None | None | None | None | None |
| 100°C. Vacuum Stability Test: cc. gas hours | 0.85 | 5.69 | 0.30 | 4.0 | 0.73 |
| 120°C. Vacuum Stability Test: cc. gas hours | 40 | 40 | 40 | 40 | 4.57 |
| | 11 / 1 | 11 / 24 | 0.36 | 5.60 | 10.77 2 |
| | | | 1.0 | 4.0 | 4.0 |

^b 1.00 gm. sample used.

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CHAPTER IV

Table II (Continued)

Explosive and Stability Characteristics of High Nitrogen Compounds.

| Test | Sensitivity to Impact, 2 kg., wt., cc. fall | Sand Test | Compound # | | | | |
|---|--|-----------|--|----------------------------|--------------------------|------------------------|-----------------------|
| | | | Guanyl Nitroaminoguanidine and nitrourea | Sulfoxide and nitrourea | Nitrate and nitrourea | Diguanazole Oxalate | Cyanuric Hydrazide |
| Brittleness, gm. sand crushed | 100 | / | 20 | 95 | 100 | / | 80 |
| Initiated at 1/16 in. | | | | | | | |
| 0.30 g. Hg(OSC) ² / ₂ | 3.3 | 55.2 | None | None | None | None | 4.7 |
| 0.25 g. Hg(OSC) ² / ₂ | 25.4 | None | None | None | None | None | |
| Sensitivity to Initiation, gm. Hg(OSC) ² / ₂ | | 0.23 | | | | | |
| Decomposition Temperature | | | | | | | |
| Temp. to cause decom. in 5 sec., °C. | 295 | 140 | 290 | 340 | 340 | 260 | |
| 100°C. Heat Test, Loss, first 48 hrs., % | 0.13 | 4.19 | 0.38 | 0.26 | 0.13 | 0.27 | 0.02 |
| Loss, second 48 hrs., % | 0.22 | 18.51 | 0.34 | None | None | None | |
| Explosion at 100 hrs. | None | None | None | None | None | None | |
| 100°C. Vacuum Stability Test: cc. gas hours | 0.91 | 0.40 | 0.40 | 0.40 | 0.40 | 0.40 | |
| 120°C. Vacuum Stability Test: cc. gas hours | 8.22 | 4.0 | 0.55 | 0.50 | 0.50 | 0.50 | 0.09 |

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